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(12) **Patent Application:** (11) **CA 2092730**

(54) METHOD OF PRODUCING THREE-DIMENSIONALLY SURFACE-STRUCTURED LININGS FORWALL AND FLOOR SURFACES AND STRUCTURE PASTE THEREFOR

(54) METHODE DE FABRICATION DE REVETEMENTS MURAUX ET DE SOL A RENFORT TRIDIMENSIONNEL DE SURFACE ET PATE ASSOCIEE

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ABSTRACT:

Abstract
A method is described for producing structured wallpapers in which a

PVC-free and plasticizer-free structure paste on
The basis or inorganic and/or organic fillers and a polymer dispersion of a vinyl acetate copolymer is used. Noncrystallizing sorbite syrup or ethylene glycol as processing retarding agents, paraffin dispersion as hydrophobing agent and micropearls and/or hollow microbeads for increasing the specific volume may also be added to the structure composition.

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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(19)(CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Method of Producing Three-Dimensionally Surface-Structured Linings for Wall and Floor Surfaces and Structure Paste Therefor

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1

Method of producing three-dimensionally surface-structured linings for wall and floor surfaces and structure paste therefor

The invention relates to a method of producing three-dimensionally surface-structured coverings or linings for wall and floor surfaces, in particular for producing structured wallpaper according to the preamble of claim 1. The invention further relates to a structure paste for use in this production.

Floor linings, wall linings and in particular wallpapers having a structured relief-like surface are known. For producing the relief-like structures, in known methods either blowing-agent-free compact plastisols or blowing-agent-containing foam plastisols are used, in each case on the basis of polyvinyl chloride (PVC).

Depending on the type of structure to be formed, the plastisol paste is applied by known application methods, in particular printing methods, to a suitable substrate web which may consist of various materials, in particular plastic materials, but in the case of structured wallpaper is usually a raw wallpaper. Suitable methods of application are the rotary screen printing method, the flat screen printing method, the rotogravure method, the squeeze rotogravure method, letterpress printing method, coating methods and spraying methods.

After their solidification on the substrate web PVC plastisol pastes have properties which have led them to be generally used for the purpose in question here. They have

a good resistance to light, are highly resistant to washing, scratch-resistant, and even in the solidified state remain adequately soft and flexible, can be worked to relatively lightweight structures by employing blowing agents, are resistant to wear and also flame-resistant. The PVC plastisols however also have some disadvantages. Thus, for the gelation and foaming they require relatively high processing temperatures in the range of 180°C to 230°C and furthermore they reduce the breathing activity of the walls and are sensitive to nicotine (discolouring). However, the greatest disadvantage of PVC plastisols is their chemical origin because they are chlorinated compounds which can lead to environmental problems. The polyvinyl chlorides are essentially rot proof and consequently can generally only be disposed of by burning. When this is done they give off harmful hydrochloric acid vapours, which by the way also occure in the case of fire, and can become a considerable hazard to humans. Furthermore PVC plastisols fundamentally contain plasticizers, substancially phthalates, which are partially liberated during processing and require expensive collection and combustion apparatuses.

The invention is based on the problem of providing a method of producing three-dimensionally surface-structured linings or coverings for wall, ceiling and floor surfaces in which structuring pastes are used which are essentially free from PVC and plasticizers, can be worked by the hitherto usual application methods without any problems and lead to high product quality. The objective of the invention is also to make available a particular substantially PVC-free and plasticizer-free structure paste for producing surface structured linings.

As regards the method, this problem is solved according to the invention fundamentally by the characterizing features of claim 1. A suitable structure paste is characterized fundamentally by claim 8.

For simplicity, hereinafter the invention will be described only in its application to the production of structured wallpapers; it will be clear to the person skilled in the art that the production method described can be applied likewise to other structured articles and thus in particular is suitable also for producing other wall and floor coverings and linings. Also, the substrate is in no way restricted to the raw wallpaper usually employed when making structured wallpaper. The substrate may consist of a great variety of materials, in particular raw wallpapers precoated in suitable manner may also be employed for producing structured wallpapers.

It has been found in extensive tests that high-quality structured surfaces can be obtained using structure pastes based on polymer dispersions of vinyl acetate copolymers and containing suitable fillers and pigments in an aqueous system. The aqueous system has the advantage that the structure paste can be solidified by simple drying or evaporation and no harmful vapours are formed. The drying may take place at temperatures between 40 and 200°C and this is another advantage compared with the use of PVC plastisols.

The structure paste according to the invention may also be worked using the application methods mentioned at the beginning hitherto usual for PVC plastisols. A further surface finishing of the solidified structures, for example by imprinting, painting, flocculation or the like, is readily possible.

A polymer dispersion on the basis of a vinyl acetate-ethylene copolymer (EVA) available as a 50 to 55 % plasticizer-free dispersion of said copolymer in water has been found particularly suitable for the structure paste according to the invention. This dispersion leads to good flow properties of the structure paste and ensures an adequate binding of the other components of the paste with respect to each other; it exhibits good adhesion to the substrate and after drying leads to a permanently flexible structure.

Other polymer dispersions have been found suitable, for example on the basis of vinyl acetate maleic acid di-n-butyl ester and vinyl acetate-acrylic acid ester.

A fundamental composition of the structure preparation according to the invention may reside in that it contains 0.8 2.0 parts by weight of a 50 - 55 % polymer dispersion for 1 part by weight inorganic and/or organic fillers.

As organic filler for the structure paste, principally ungelatinized starch can be used, preferably potato starch. The ungelatinized or non-agglutinated starch has a good filling power without the structure composition becoming heavier because the starch is lighter than the inorganic fillers. Furthermore, it is biologically easily and completely decomposible and this has a positive effect on the decomposibility of the structure paste. Since the ungelatinized starch forms a unit with the inorganic fillers, irrespective of whether the inorganic fillers are calcium carbonates or aluminium hydroxides, it can be regarded as a partial substitute for inorganic fillers.

Moreover, the ungelatinized starch is insoluble in cold water and begins to dissolve only with rising temperatures. This property has production technical advantages. The drying temperature and the drying duration can be chosen so that the starch particles at their surface are slightly initially dissolved by the temperature and the moisture of the mixture and combine with each other and with the other fillers to form a unit. This gives a better strength of the structure composition.

In addition, the starch binds a considerable proportion of the water and liberates the latter slowly during drying. This prevents rapid evaporation, which could lead to formation of bubbles.

When using starch the total fillers contain expediently at least 10 % by weight, preferably however 25 - 40 % by weight, ungelatinized starch as organic filler. The ungelatinized starch is present in powder form, preferably with a grain size of 10 - 100 µm.

Possible inorganic fillers for the structure composition are primarily aluminium hydroxide ($Al(OH)_3$) and calcium carbonate ($CaCO_3$). However, a certain addition of titanium dioxide (TiO_2) may also be advantageous as additional white pigment. The amount of titanium dioxide used may be up to 10 % by weight of the total inorganic and/or organic fillers.

The aluminium hydroxide as filler is preferably used with a grain size of 20 - 25 µm. The calcium carbonate preferably has a grain size distribution of 5 - 30 µm and an oil number of 15. In the case of titanium dioxide, preferably the rutile modification is employed. Deviations from the filler specifications above are however possible.

It has further been found extremely advantageous to add to the system a certain amount of an organic processing retarder. It has been found that the addition of 1 - 8 % by weight non-crystallizing sorbite syrup, with respect to the total paste, is very advantageous for the working thereof because in addition to the working retardation the viscosity of the structure paste is also positively influenced.

The non-crystallizing sorbite syrup may possibly be replaced by ethylene glycol or other organic solvents with corresponding properties. Thus, it has been found that the addition of 1 - 5 % by weight ethylene glycol, with respect to the total paste, is also advantageous for the working thereof in certain cases.

It may also be advantageous to add hydrophobing agents to the structure paste to impart to the structured wallpaper to be made a water-repellent character to a certain extent. It has been found that this can also be achieved by addition of 1 - 3 % by weight paraffin dispersion with respect to the total paste.

To reduce the specific weight of the dried structure paste and to intensify the structure formation thereof during drying as well, appropriate additives may be added to the structure paste in relatively small amounts by weight.

To enable the specific volume of the structure paste to be increased during the processing, in particular during the drying, it has been found advantageous to add to the total paste about 1 - 8 % by weight of so called microperls. Microperls are microcapsules which are filled with a blowing agent and have a diameter of about 10 - 30 µm.

consisting of thermoplastic plastic, and at 120 - 140°C they expand to several times their volume. These micropearls have for example polymer shells on the basis of methylmethacrylate or also an acrylonitrile copolymer. Preferably, forms are used which have an expansion ratio of about 20. In the structure paste according to the invention these micropearls partially perform the function of the blowing agent in the conventional PVC plastisols.

Moreover, to reduce the specific weight of the fillers or increase the specific volume of the dried paste, a proportion of about 1 - 5 % by weight so-called hollow microbeads may be added to the total paste. These are expanded hollow polymer beads, in the surface of which inorganic fillers are advantageously embedded. The diameter of such hollow microbeads is preferably in the range of 10 - 80 µm and their specific volume is about 0.15 g/cm³. Due to the polymer material of the microbead walls and the inorganic filler particles attached thereto, the hollow microbeads are practically a mixed organic-inorganic filler of very high specific volume. The person skilled in the art is familiar with the viscosity which a structure paste must approximately have to permit working in a specific application method. This viscosity can be regulated with the paste according to the invention by appropriate addition of water.

Of course, colour pigments or dyes may for example also be added to the structure paste according to the invention to influence the outer appearance thereof. It may also be necessary for the working to add to the composition small amounts of biocides or a defoamer, should this prove necessary. The person skilled in the art is familiar with such additives.

Two preferred composition types of the structure paste according to the invention are as follows, in parts by weight:

240-360 p.b.w. of a 50-55 % plasticizer-free EVA dispersion
5- 50 p.b.w. non-crystallizing sorbite syrup
10- 60 p.b.w. microbeads
300 p.b.w. $Al(OH)_3$ and ungelatinized starch
5- 35 p.b.w. water as viscosity adjusting agent.

or:

240-360 p.b.w. of a 50-55 % plasticizer-free EVA dispersion
6- 30 p.b.w. ethylene glycol
6- 40 p.b.w. micropearls
330 p.b.w. $Al(OH)_3$ and/or $CaCO_3$
6- 30 p.b.w. hollow microbeads
25- 30 p.b.w. water as viscosity adjusting agent.

Up to 30 % by weight titanium dioxide of the rutile type may also be added to these compositions. In addition, the compositions, as mentioned above, may also be supplemented by colour pigments, dyes, defoamers, biocides and similar additives to be used in small amounts.

A structure paste of the compositions set forth above meets all the demands made on it. It has a good resistance to light, is highly weatherproof, scratch-proof, hardwearing, remains soft and flexible, and in addition can be made with relatively light weight. In addition, it is hardly inflammable, this being due to the relatively high content of aluminium hydroxide. Compared with the conventional PVC plastisol structures it has the additional advantages that it is free from PVC and plasticizer, has a good water vapour permeability and is insensitive to nicotine, and on

combustion does not give off any chlorine-containing compounds, in particular no hydrochloric acid vapours. Furthermore, it does not contain any solutions which are troublesome during working or would have to be collected and may be solidified at relatively low temperatures, leading on the whole to a saving in energy during working. Finally, the structure paste according to the invention is also easily biologically decomposible.

Examples of Embodiment

Example 1:

A structure paste was mixed together from the starting materials in the amounts given below:

280 p.b.w.	of a 50-55 % plasticizer-free EVA dispersion
200 p.b.w.	$Al(OH)_3$ having a
	grain size distribution of 20-25 µm
100 p.b.w.	of an undelatinized starch
20 p.b.w.	TiO_2 of rutile type
37.5 p.b.w.	micropearls
45 p.b.w.	of a non-crystalline sorbite syrup
40 p.b.w.	paraffin dispersion and
10 p.b.w.	water as viscosity adjusting agent.

The EVA dispersion, the non-crystallizing sorbite syrup and the water were placed in an agitating vessel and slowly agitated. During the agitation the unpelatinized starch, the micropearls, the aluminium hydroxide, the titanium dioxide and the paraffin dispersion were slowly added in succession. After about 30 min. agitating time the paste was ready to use.

On a polymer non-woven fabric as substrate, having a weight per unit area of 50 g/m² and a width of 110 cm, a wallpaper structure was applied with the paste in the screen printing method at a rate of 40 m/min. This structure was dried at about 150°C for 35 sec. The structured wallpaper thus produced met all the demands made on it.

Example 2:

A structure paste was mixed together from the starting materials in the amounts given below:

330 p.b.w.	of a 50-55 % plasticizer-free EVA dispersion
200 p.b.w.	$Al(OH)_3$ having a
	grain size distribution of 20-25 µm
100 p.b.w.	of an ungelatinized starch
15 p.b.w.	micropearls
10 p.b.w.	of a non-crystalline sorbite syrup
7.5 p.b.w.	paraffin dispersion and
25 p.b.w.	water as viscosity adjusting agent.

The EVA dispersion, the non-crystallizing sorbite syrup and the water were placed in an agitating vessel and slowly agitated. During the agitation, the ungelatinized starch, the micropearls, the aluminium hydroxide and the paraffin dispersion were slowly added in succession. After about 30 min. agitating time the paste was ready to use.

On a polymer non woven fabric as substrate, having a weight per unit area of 50 g/m² and a width of 110 cm, a wallpaper structure was applied with the paste in the gravure method at a rate of 40 m/min. This structure was dried at about 150°C for 35 sec. The structured wallpaper thus produced met all the demands made on it.

Example 3:

A structure paste was mixed together from the starting materials in the amounts given below:

300 p.b.w.	of a 50 55 % plasticizer-free EVA dispersion
30 p.b.w.	water
10 p.b.w.	ethylene glycol
7 p.b.w.	micropearls having a grain diameter of 10 - 20 µm and an expansion ratio of 20
130 p.b.w.	$Al(OH)_3$ having a grain size distribution of 20-25 µm
100 p.b.w.	$CaCO_3$ having a grain size distribution of 5-30 µm
7.5 p.b.w.	TiO_2 of rutile type
12 p.b.w.	hollow microbeads having a diameter of 10-80 µm.

The EVA dispersion, the ethylene glycol and water were placed in an agitating vessel and slowly agitated. During the agitation the micropearls, the aluminium hydroxide, the calcium carbonate, the titanium dioxide and the hollow microbeads were slowly added in succession. After about 30 min. agitating time the paste was ready to use.

On a polymer non-woven fabric as substrate, having a weight per unit area of 50 g/m² and a width of 110 cm, a wallpaper structure was applied with the paste in the rotary screen printing method at a rate of 40 m/min. This structure was dried at about 150°C for 35 sec. The structured wallpaper thus produced met all the demands made on it.

Claims

1. Method of producing three dimensionally surface-structured linings for wall and floor surfaces, in particular structured wallpapers, in which a structure paste is applied by means of a suitable application method in desired structure to a substrate web and then solidified on the substrate web, characterized in that a structure paste is used on the basis of a vinyl acetate-copolymer dispersion which contains inorganic and/or organic fillers and if necessary diluting agents.

2. Method according to claim 1, characterized in that a structure paste is used of which the total fillers contain a proportion of at least 10 % by weight ungelatinized starch as organic filler.

3. Method according to claim 1 or 2, characterized in that as diluting agent water is employed, with which the structure paste is adjusted to a suitable working viscosity.

4. Method according to at least one of claims 1 to 3, characterized in that the application of the structure paste to the substrate path is carried out by the rotary screen printing method, the flat screen printing method, the rotogravure method, the squeeze gravure method, the letterpress method, a coating method or a spraying method.

5. Method according to at least one of claims 1 to 4, characterized in that the structure paste is

solidified on the substrate web by drying.

6. Method according to claim 5, characterized in that the drying takes place at temperatures of 40°C to 200°C.

7. Method according to at least one of claims 1 to 6, characterized in that the solidified structure paste is subjected to a further surface finishing, in particular an imprinting, painting and/or flocculation.

8. Structure paste for producing three-dimensionally surface-structured linings for wall and floor surfaces, in particular structured wallpapers, characterized by a mixture containing a polymer dispersion on the basis of a vinyl acetate copolymer, inorganic and/or organic fillers and if necessary solvents and/or diluents.

9. Structure paste according to claim 8, characterized in that the polymer dispersion is a plasticizer-free dispersion of a vinyl acetate-ethylene copolymer (EVA).

10. Structure paste according to claim 8 or 9, characterized in that it contains ungelatinized starch as organic filler.

11. Structure paste according to at least one of claims 8 to 10, characterized in that the inorganic fillers are substantially $Al(OH)_3$ and/or $CaCO_3$.

12. Structure paste according to at least one of claims 8 to 11, characterized in that the fillers include up to 10 % by weight TiO_2.

13. Structure paste according to at least one of claims 8 to 12, characterized in that it contains 0.8 to 2.0 parts by weight of a 50-55 % polymer dispersion for 1 part by weight inorganic and/or organic fillers.

14. Structure paste according to at least one of claims 10 to 13, characterized in that the total filler contains 25-40 % by weight ungelatinized starch as organic filler and as residual filler substantially $Al(OH)_3$ as inorganic filler.

15. Structure paste according to at least one of claims 8 to 14, characterized in that it contains as processing retardation agent non-crystallizing sorbite syrup or ethylene glycol.

16. Structure paste according to claim 15, characterized in that it contains sorbite syrup in an amount of 1 to 8 % by weight with respect to the total paste.

17. Structure paste according to at least one of claims 8 to 16, characterized in that as expansion agent it contains micropearls.

18. Structure paste according to claim 16, characterized in that the amount of micropearls is 3 to 8 % by weight with respect to the total paste.

19. Structure paste according to claim 9, containing substantially:

240 360 p.b.w. of a 50-55 % plasticizer-free EVA dispersion
5- 50 p.b.w. non-crystallising sorbite syrup
10- 50 p.b.w. micropearls
300 p.b.w. $Al(OH)_3$ and ungelatinized starch
5- 30 p.b.w. water as viscosity adjusting agent.

20. Structure paste according to claim 19, characterized in that it contains 100 p.b.w. ungelatinized starch.

21. Structure paste according to claim 9, containing substantially:
240-360 p.b.w. of a 50 55 % plasticizer-free EVA dispersion
5- 30 p.b.w. ethylene glycol
6- 30 p.b.w. micropearls
230 p.b.w. $Al(OH)_3$ and/or $CaCO_3$
6 30 p.b.w. hollow microbeads
25- 35 p.b.w. water as viscosity adjusting agent.

22. Structure according to claim 19, 20 or 21, characterized in that it contains 5-25 p.b.w. paraffin dispersion.

23. Structure paste according to claim 19, 20, 21 or 22, characterized in that it additionally contains 5-30 p.b.w. TiO_2 of the rutile type.

24. Structure paste according to claims 19, 20, 22 and 23, containing substantially:

280 p.b.w.	of a 50-55 % plasticizer free EVA dispersion
200 p.b.w.	$Al(OH)_3$ having a grain size distribution of 20-25 µm
100 p.b.w.	of an ungelatinized starch
20 p.b.w.	TiO_2 of rutile type
37.5 p.b.w.	microperle having a grain diameter of 10-20 µm and an expansion ratio of 20
45 p.b.w.	of a non-crystallizing sorbite syrup
20 p.b.w.	paraffin dispersion and
10 p.b.w.	water as viscosity adjusting agent.

25. Structure paste according to claims 19, 20 and 22, containing substantially:

320 p.b.w.	of a 50-55 % plasticizer free EVA dispersion
200 p.b.w.	$Al(OH)_3$ having a grain size distribution of 20-25 µm
100 p.b.w.	of an ungelatinized starch
15 p.b.w.	microperle having a grain diameter of 10-20 µm and an expansion ratio of 20
10 p.b.w.	of a non-crystalline sorbite syrup
7.5 p.b.w.	paraffin dispersion and
25 p.b.w.	water as viscosity adjusting agent.

26. Structure paste according to claims 21 and 23, containing substantially:

300 p.b.w.	of a 50-55 % plasticizer-free EVA dispersion
30 p.b.w.	water
10 p.b.w.	ethylene glycol
7 p.b.w.	micropearls having a grain diameter of 10-30 µm and an expansion ratio of 30
130 p.b.w.	$Al(OH)_3$ having a grain size distribution of 20 25 µm
100 p.b.w.	$CaCO_3$ having a grain size distribution of 5-30 µm
7.5 p.b.w.	TiO_2 of rutile type
12 p.b.w.	hollow microbeads having a diameter of 10-80 µm.

37. Structure paste according to at least one of claims 8 to 36, characterized in that it additionally contains dyes, colour pigments, biocides and/or defoamers.

38. Use of a structure paste according to at least one of claims 8 to 37 for producing structured wallpapers.

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PATENT AGENTS

2092730

Abstract

A method is described for producing structured wallpapers in which a PVC-free and plasticizer-free structure paste on the basis of inorganic and/or organic fillers and a polymer dispersion of a vinyl acetate copolymer is used. Non crystallizing sorbite syrup or ethylene glycol as processing retarding agents, paraffin dispersion as hydrophobing agent and micropearls and/or hollow microbeads for increasing the specific volume may also be added to the structure composition.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente